

Appendix A

Principles of — Polymerization —

SECOND EDITION

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Isolic Chain Polymerization

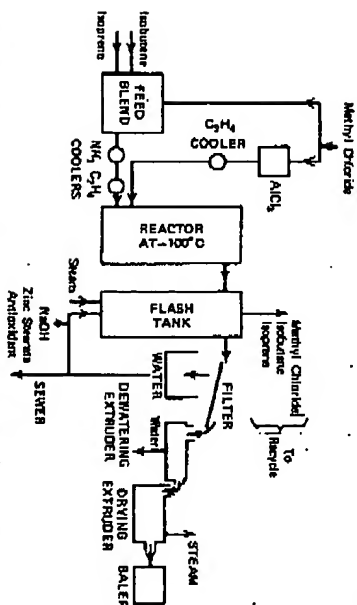


Fig. S.3 Flow diagram for commercial synthesis of butyl rubber. After [85] by permission of Wiley, Inc.

three quarters of all butyl rubber is used for inner tire tubes (which are still used in almost all nonpassenger tires). Other uses include cable insulation, vibration dampers, pharmaceutical stoppers, and automotive parts.

S.3 ANIONIC POLYMERIZATION OF THE CARBON-CARBON DOUBLE BOND

Anionic chain polymerizations show many of the same characteristics as cationic polymerizations, although there are a number of distinct differences [4,96-100]. The propagating species are anionic ion pairs and free ions with relative concentrations which depend on the reaction media as in cationic polymerization. Although anionic polymerizations generally proceed rapidly at low temperatures, they are usually not as temperature-sensitive as cationic polymerizations. Further, most anionic polymerizations possess positive E_a values and proceed well at ambient temperatures and higher. Anionic polymerizations are easier to understand, since the identities of the initiating species and counterions are much better established.

Termination occurs by transfer of a positive fragment, usually a proton, from the known. Many anionic chain polymerizations are, however, devoid of any termination reaction. Such polymerizations without termination comprise a significant departure from the corresponding behaviors in radical and cationic polymerizations.

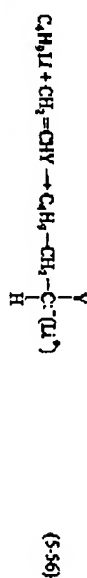
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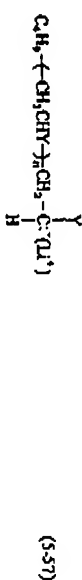
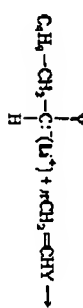
S.3a Initiation

S.3a-1 Nucleophilic Initiators

A variety of basic initiators have been used to initiate anionic polymerization [4,96,98,99]. These include covalent or ionic metal amides such as NaNH_2 and $\text{LiN}(\text{C}_2\text{H}_5)_3$ [101,102], alkoxides, hydroxides, cyanides, phosphines, and amines [103,104]; organometallic compounds such as $n\text{-C}_4\text{H}_9\text{Li}$, PhMgBr , [107]. Initiation usually involves the addition to monomer of a nucleophilic (base) B^- . Alkyl-lithium initiators are among the most useful, being employed commercially in the polymerization of butadiene and isoprene. Initiation proceeds by addition of the initiator to monomer:

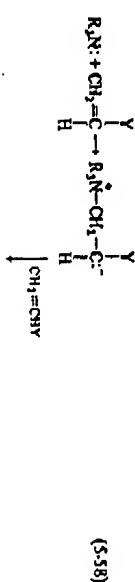


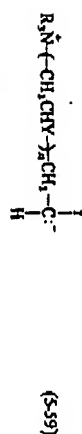
followed by propagation,



The extensive use of alkyl-lithium initiators is due to their solubility in hydrocarbon solvents. Alkyls or aryls of the other alkali metals are poorly soluble in hydrocarbon. Their use in polar solvents is limited by their being sufficiently reactive (due to the more ionic C-metal bond) to attack such compounds as ethers. The latter problem can be overcome by using less reactive anions as in benzylpotassium, triphenylmethylsodium, and cumylpotassium.

In the relatively few anionic polymerizations initiated by neutral nucleophiles such as an amine,



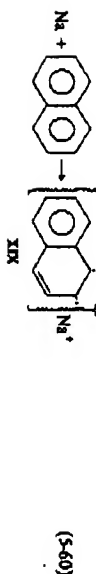


The propagating species is proposed to be a *switterion*. Such propagating species have the glaring deficiency of requiring increasing charge separation as propagation proceeds. Stabilization of *switterion* species may involve the positive end of one propagating chain acting as the germination end of another propagating chain [104,109]. The need for a *switterion* propagating species is avoided if initiation is proposed as occurring by hydroxide, formed by the reaction of the amine with atmospheric water (Sec. 5-3a-1).

The initiator required to polymerize a monomer depends on the reactivity of the monomer toward nucleophilic attack. Monomer reactivity increases with increasing ability to stabilize the carbocation charge. Very strong nucleophiles such as amide ions or alkyl carbanions are required to polymerize monomers, such as styrene and 1,3-butadiene, with relatively weak electron-withdrawing substituents. Weaker nucleophiles (alkoxide ions) can polymerize monomers such as acrylonitrile, methyl methacrylate, and methyl vinyl ketone, with strongly electron-withdrawing substituents. A monomer, such as methyl α -cyanoacrylate, with two such substituents can be polymerized with very mild nucleophiles such as Br^- , CN^- , amines, phosphines, and possibly even water [104,108].

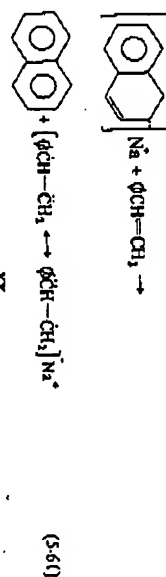
5-3a-2 Electron Transfer

Szwarc and co-workers have studied the interesting polymerizations initiated by aromatic radical-ions such as sodium naphthalene and sodium triphenyl [[10]. Initiation proceeds by the prior formation of the active initiator, the naphthalene radical-anion ($\text{X}^{\cdot-}$)

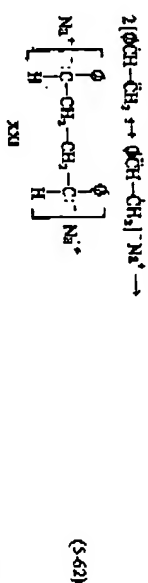


The reaction involves the transfer of an electron from the alkali metal to naphthalene. The radical nature of the radical anion has been established from electron spin resonance measurements and the carbocation nature by their reaction with carbon tetrachloride to form the carbonylic acid derivative. The equilibrium in Eq. 5-60 depends almost on the electron affinity of the hydrocarbon and the donor properties of the solvent. Sodium naphthalene, for example, is formed quantitatively in tetrahydrofuran, but in dilution with hydrocarbons results in precipitation of sodium and regeneration of naphthalene. For the less electropositive alkali earth metals, an even more powerful solvent such as hexamethylphosphoramide is needed. The electron affinity of naphthalene is greater than that of triphenyl

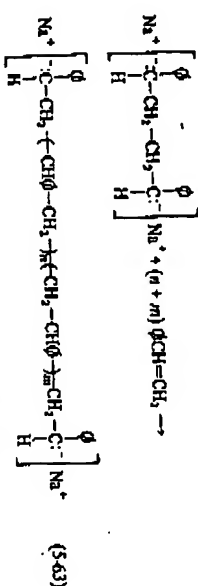
The naphthalene anion-radical (which is colored greenish-blue) transfers an electron to a monomer such as styrene to form the styryl radical-anion (XX_1).



The styryl radical-anion is shown as a resonance hybrid of the forms wherein the anion and radical centers are alternately on the α - and β -carbon atoms. The styryl radical-anion dimerizes to form the dication (DCK).



That this reaction occurs is shown by electron spin resonance measurements, which indicate the complete disappearance of radicals in the system immediately after the addition of monomer. The dimerization occurs to form the styryl dication instead of $\cdot\text{C}_6\text{H}_5\text{CH}=\text{CHCH}_2\text{CH}_2\cdot$, since the former is much more stable. The styryl dication, $\text{C}_6\text{H}_5\text{CH}=\text{CHCH}_2\text{CH}_2^+$, is not colored red (the same as styryl monocation) formed by dimerization to form red colored red (the same as styryl monocation) formed by dimerization such as *p*-nonylium). Anionic propagation occurs at both carbonion ends of the styryl dication.



Although the suggestion that the styryl anion-radical adds a few monomer molecules prior to dimerization has not been discounted, the reaction kinetics (Sec. 5-3d) clearly show that better than 99% of the propagation occurs through the dianion.

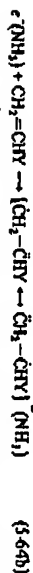
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Electron-transfer initiation from other radical-anions, such as those formed by reaction of sodium with nonreducible ketones, azomethines, nitriles, azo and azoxy compounds, has also been studied [112]. In addition to radical-anion, initiation by electron transfer has been observed when one uses certain alkali metals in liquid ammonia. Polymerizations initiated by alkali metals in liquid ammonia proceed by two different mechanisms. In some systems, such as the polymerizations of styrene and methacrylonitrile by potassium, the initiation is due to anide ion formed in the system [101, 113]. Such polymerizations are analogous to those initiated by alkali anides. Polymerization in other systems cannot be due to anide ion. Thus polymerization of methacrylonitrile by lithium in liquid ammonia proceeds at a much faster rate than that initiated by lithium anide in liquid ammonia [114]. The mechanism of polymerization is considered to involve the formation of a solvated electron.



Such ammonia solutions are noted by their characteristic deep blue color. The solvated electron is then transferred to the monomer to form a radical-anion.



The radical anion proceeds to propagate in the same manner as discussed above for initiation by sodium naphthalene. (Polymerizations in liquid ammonia are very different from those in organic solvents in that free ions probably constitute the major portion of propagating species.)

Electron-transfer initiation also occurs in heterogeneous polymerization involving dispersions of an alkali metal in monomer. Initiation involves electron transfer from the metal to monomer followed by dimerization of the monomer radical-anion to form the propagating dianion [100, 112]. The rate of initiation is dependent on the surface area of the metal, since the reaction is heterogeneous. Increased surface area of metal is achieved by small particle size of the metal dispersion or the use of a thin coating (nitrocellulose) of the metal on the inside walls of the reaction vessel.

Initiation by ionizing radiation occurs by electron transfer. Some component of the reaction system, either the solvent or monomer, undergoes radiolysis



to yield a radical-cation and solvated electron. If a monomer with electron-withdrawing substituents is present, polymerization occurs by addition of the electron to monomer followed by dimerization and propagation [112, 115-117]. That initiation involves electrons is indicated by inhibition of polymerization in the presence of electron scavengers such as N_2O and Se_2 .

Electroinitiated polymerization proceeds by direct electron addition to monomer to generate the monomer anion-radical, although initiation in some systems may involve the formation of an anionic initiating species by electrolytic reaction of some component of the reaction system (most often, the electrolyte) [112, 118, 119].

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5-3b Termination

5-3b-1 Polymerizations Without Termination

Termination of a propagating anion by combination with the counterion occurs only in a few instances (e.g., in electroinitiated polymerization when the contents of the anode and cathode chambers are mixed and in initiation by kinking radical ions). Termination by combination of the anion with a metal counterion does not take place. Many anionic polymerizations, especially of nonpolar monomers such as styrene and 1,3-butadiene, take place under conditions in which there are no effective termination reactions. Propagation occurs with complete consumption of the monomer. The propagating anionic centers remain intact because transfer of a proton (or other positive species) from the solvent does not occur. Such nonterminated polymer anions are referred to as living polymers. Living polymers are produced as long as one employs solvents (e.g., tetrahydrofuran, 1,2-dichloroethane, benzene), which are inactive in terms of terminating the propagating anion by chain transfer. The polymerization of styrene by anide ion in liquid ammonia, the first anionic system to be studied in detail [113], is one of the few anionic polymerizations where chain transfer to solvent is extensive.

The nonterminating character of living polymerizations is apparent in several different ways. Many of the propagating carbanions are colored. If a system is highly

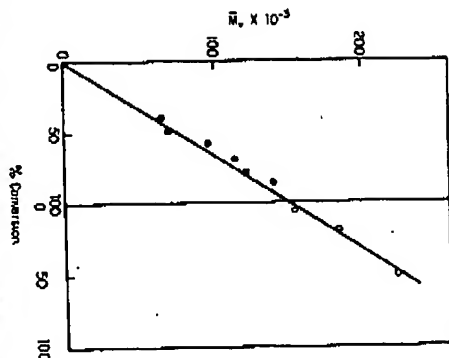


Fig. 5-6. Dependence of polymer molecular weight on percent conversion of the anionic polymerization of methyl methacrylate. \bullet represents polymerization initiated by CaH_2Li and \circ represents polymerization of living anions by addition of a second batch of monomer. After [120] (by permission of Wiley, New York).

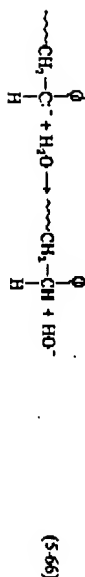
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purified so that impurities are absent, the color of the cation is observed to persist throughout polymerization and does not disappear or change at 100% conversion. Further, after 100% conversion is reached, additional polymerization can be effected by adding more monomer to the living polymer system. The added monomer is also polymerized quantitatively. The molecular weight of the living polymer is increased accordingly as the number of polymer molecules does not change. Figure 5-4 shows this effect for the polymerization of methyl methacrylate initiated by *n*-butyllithium [120].

5-3b-2 Termination by Impurities and Deliberately Added Transfer Agents

Anionic polymerizations are usually carried out under high vacuum or in an inert atmosphere with rigorously cleaned reagents and glassware since trace impurities lead to termination. Moisture adsorbed on the surface of glassware is usually removed by flaming under vacuum or working with a living polymer solution. Oxygen and carbon dioxide from the atmosphere add to propagating carbanions to form peroxy and carboxyl anions. These are normally not reactive enough to continue propagation. (The peroxy and carboxyl anions usually are finally obtained as HO and HOOC groups when a proton donor is subsequently added to the polymerization system.) Any moisture present terminates propagating carbanions by proton transfer,



The hydroxide ion is usually not sufficiently nucleophilic to re-initiate polymerization and the kinetic chain is broken. Water has an especially negative effect on polymerization, since it is an active chain transfer agent. For example, $G_{p,0}$ is approximately 10 in the polymerization of styrene at 25°C with sodium naphthalene [121], and the presence of even small concentrations of water can greatly limit the polymer molecular weight and polymerization rate. The adventitious presence of other proton donors may not be as much of a problem. Ethanol has a transfer constant of about 10^{-3} . Its presence would not prevent the formation of high polymer because transfer would be slow, although the polymer would not be living.

Living polymers are usually terminated by the deliberate addition of a chain transfer agent such as water or alcohol to the reaction system after all of the monomer has reacted.

5-3b-3 Hydride Elimination

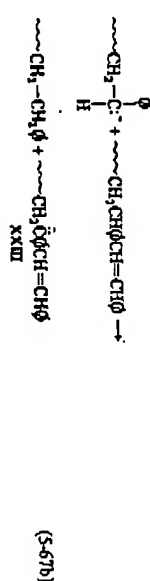
In the absence of terminating agents the concentration of carbanion centers in a solution of living polystyrene decreases very slowly. Termination occurs over a period of days or weeks by hydride elimination:

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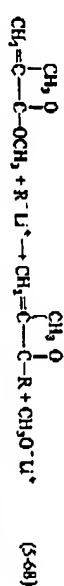
The sodium hydride is more than sufficiently reactive to reinitiate polymerization. However, termination of the kinetic chain occurs when the allylic hydrogen of the unsaturated end group in XXII is abstracted by a propagating carbanion,



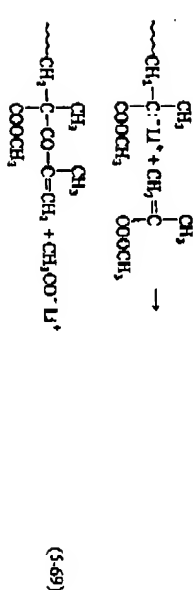
to yield the unreactive 1,3-diphenylallyl anion (XXIII).

5-3b-4 Terminating Reactions of Polar Monomers

Our understanding of the anionic polymerizations of polar monomers, such as methyl methacrylate, methyl vinyl ketone, and acrylonitrile, is much less than for the nonpolar monomers. The polar monomers contain substituents that are reactive toward nucleophiles. This leads to termination and side reactions competitive with both initiation and propagation, resulting in complex polymer structures. Three different nucleophilic substitution reactions have been observed in the polymerization of methyl methacrylate [97,172,123]. Attack of the initiator on monomer

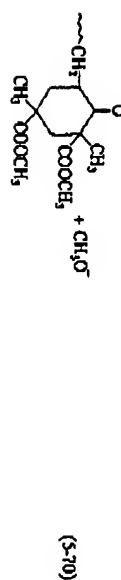
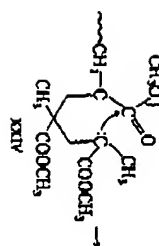


converts the active alkyl lithium to a less active alkoxide initiator. Reaction 5-68, to the extent it occurs, also changes the identity of the monomer and of the subsequently formed polymer to a mixture of methyl methacrylate and the corresponding ketone. Nucleophilic attack of the propagating carbanion on monomers



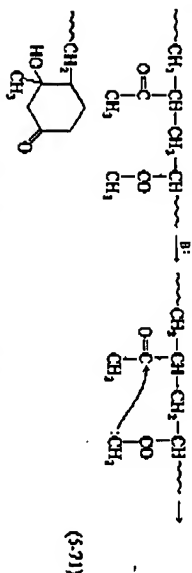
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and intramolecular "backbiting" attack.

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lower the polymer molecular weight; the polymerization rate may also be affected depending on the extent of retardation by methoxide ion. Reaction 5-68 can be avoided to a large extent by using a less nucleophilic initiator, for example, 1,1-diphenyllithium instead of *n*-butyllithium [97,124]. Lower reaction temperatures (below -50 to -70°C) and more polar solvents (ethers instead of hydrocarbons) favor normal propagation relative to Reactions 5-68, 5-69, and 5-70. Living polymerizations of acrylates and methacrylates are observed under the appropriate reaction conditions.

The polymerization of vinyl ketones is also complicated by nucleophilic attack of the initiator and propagating carbanion at the carbonyl group although the details of these reactions have not been well-established [97,125,126]. Nucleophilic attack at the carbonyl group in these polymers results in addition, while that at the ester carbonyl yields substitution. Further, Aldol-type condensation occurs when the polymer has acidic α -hydrogens,

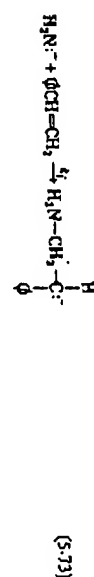


Acrylonitrile polymerization is similarly complicated by addition reactions of the initiator and propagating nucleophiles with the nitrile group [105,107,127].

5.3e Kinetics of Polymerization with Termination

The polymerization rate for an anionic system where termination occurs simultaneously with propagation follows in exactly the manner described for cationic polymer-

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esterations (Sec. 5.3d). For potassium amide initiated polymerization in liquid ammonia, initiation involves the dissociation of potassium amide followed by addition of amide ion to the first monomer unit.



The rate of initiation is given by

$$R_i = k_i [\text{H}_2\text{N}^-] [\text{M}] \quad (5-74a)$$

or

$$R_i = \frac{k_i K [\text{M}] [\text{KNH}_2]}{[\text{K}^+]} \quad (5-74b)$$

Propagation proceeds according to

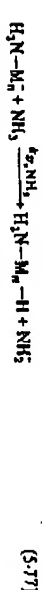


with a rate given by

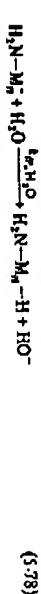
$$R_p = k_p [\text{M}^-] [\text{M}] \quad (5-76)$$

where $[\text{M}^-]$ represents the total concentration of the propagating anionic centers.

Chain transfer to solvent



is extensive but does not terminate the kinetic chain since amide ion is regenerated. Termination occurs by transfer to adventitious water,



or other impurity present. The rates of Reactions 5-77 and 5-78 are given by

$$R_{tr, \text{NH}_3} = k_{tr, \text{NH}_3} [\text{M}^-] [\text{NH}_3] \quad (5-79)$$

$$R_{tr, \text{H}_2\text{O}} = k_{tr, \text{H}_2\text{O}} [\text{M}^-] [\text{H}_2\text{O}] \quad (5-80)$$

The polymerization rate, derived in the usual manner by combining Eqs. 5-74, 5-76, and 5-80 with the assumption of a steady state for $[\text{M}^-]$, is obtained as

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$$R_p = \frac{k_p k_a [M]^2 [KNH_2]}{k_{tr} + k_p [M] + k_a [H_2O]} \quad (5-81)$$

The number-average degree of polymerization is given by

$$\bar{X}_n = \frac{1}{[M]} \frac{C_{NH_2} [NH_2] + C_{H_2O} [H_2O]}{C_{H_2O} [H_2O]} \quad (5-82)$$

5-3d Kinetics of Living Polymerization

The anionic ion initiated polymerizations in liquid ammonia are about the only anionic polymerizations studied which proceed with termination. There is little interest, theoretical or practical, in such systems. The interest in present is in living polymerizations.

5-3d-1 Polymerization Rate

The rate of polymerization in nonterminating systems is expressed simply as the rate of propagation

$$R_p = k_p [M^-] [M] \quad (5-83)$$

where $[M^-]$ is the total concentration of living anionic propagating centers. The concentration of living ends can be determined spectrophotometrically as propagating carbanions have strong absorption peaks in the visible or near ultraviolet region ($\epsilon \sim 10^3$) (110). An alternate technique is to react the solution of living polymer with a terminating agent such as water, methyl iodide, or carbon dioxide followed by analysis of the amount of terminating agent incorporated into the polymer. The use of isotopically labeled terminating agents can increase the analytical sensitivity. For many living polymerizations where adventitious terminating agents are absent and initiation is fast relative to propagation, $[M^-]$ will be given by the concentration of initiator (e.g., the concentration of sodium naphthalene). The living ends are monocations in polymerizations initiated by organometallics such as butyllithium and dianions in polymerizations initiated by electron-transfer. The two types of anions are referred to as *one-ended* and *two-ended* living anions. (Equation 5-83 does not apply if the initiation rate is of the same order of magnitude or lower than the propagation rate. More complex kinetic expressions, similar to those developed for radical and cationic polymerization would apply [128].)

Many anionic polymerizations, like their cationic counterparts, proceed too fast to be followed by the usual experimental techniques such as dilatometry. The polymerization of styrene by sodium naphthalene in tetrahydrofuran, for example, is essentially complete in seconds. *Stopped-flow* techniques are useful for studying such fast polymerizations (Sec. 5-2e-1) [110, (29,130)]. Solutions of monomer and initiator in two separate reservoirs are forced through a mixing chamber and then into a capillary tube where flow is stopped and in which reaction takes place. If

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the capillary tube is in a spectrophotometer, one can follow the initiation rate (by observing the increase in optical density at the wavelength of absorption by the propagating carbanion) and/or the polymerization rate (by the loss of monomer). The polymerization rate can also be obtained by a modification of the apparatus in which polymerization is stopped by running the contents of the capillary tube into a solvent containing a terminating agent. The reaction time is given by the ratio of the capillary volume to the flow rate. Short reaction times from 0.005 to 2 sec can be accurately studied in this manner. The conversion and, hence, R_p and k_p are obtained by analyzing the quenched reaction mixture for either polymer or unreacted monomer.

It is of interest to understand the reasons for the faster reaction rates encountered in many anionic polymerizations compared to their radical counterparts. This can be done by comparing the kinetic parameters in the appropriate rate equations (Eqs. 3-22 and 5-83). The k_p values in anionic polymerization are about the same as the k_p values in radical polymerization. Anionic k_p values may be 10^{-10} lower than in radical polymerization for very low polarity solvents while they may be 10^{-10} higher for polymerization in solvents of high polarity. The difference in the anionic and radical rates is due to the absence of termination and to the difference in the concentrations of the propagating species. The concentration of propagating radicals is 10^{-9} – 10^{-7} M, while that for propagating anions is often as high as 10^{-3} – 10^{-2} M. Thus anionic polymerization rates are higher than radical rates by a factor of 10^4 – 10^7 based only on the concentrations of propagating species.

5-3d-2 Effects of Reaction Media

The propagation rate constant and the polymerization rate for anionic polymerization are drastically affected by the nature of both the solvent and the species. Thus, the data in Table 5-9 show the pronounced effect of solvents in the polymerization of styrene by sodium naphthalene (3×10^{-3} M) at 25°C. The propagation rate constant is increased by two and three orders of magnitude in tetrahydrofuran and 1,2-dimethoxyethane, respectively, compared to the rate constants in benzene or dioxane. The polymerization is much faster in the more polar solvents. That the dielectric constant is not a quantitative measure of the solvating power of a solvent is shown by the higher reaction rate in 1,2-dimethoxyethane compared to tetra-

Table 5-9 Effect of Solvent on Anionic Polymerization of Styrene^a

Solvent	Dielectric Constant (ϵ)	k_p (liter/mole-sec)
Benzene	2.2	2
Dioxane	2.2	5
Tetrahydrofuran	7.6	550
1,2-Dimethoxyethane	5.5	3,800

^aData from [311].

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hydrofuran (THF). The faster rate in the former must be due to a specific solvation effect of the ether group in THF. The same effect must be responsible for the higher reaction rate in dioxane compared to benzene.

The increased rate observed with increasing solvating power of the reaction medium is due mainly to the increased fraction of free ions relative to ion pairs. The k_p values in Table 5-9, calculated from Eq. 5-83, are apparent rate constants (Sec. 5-2e-2). It would be much more informative if one obtained the individual propagation rate constants for the free ions and ion pairs as well as information on the relative amounts of the two types of propagating species.

5-36-2a. Evaluation of Individual Propagation Rate Constants for Free Ions and Ion Pairs. The rate of polymerization is appropriately expressed as the sum of the rates for the free propagating anion P^- and the ion pair $P^-(C^+)$:

$$R_p = k_p^-[P^-][M] + k_p^+[P^-(C^+)] [M] \quad (5-84)$$

where k_p^- and k_p^+ are the propagation rate constants for the free ion and ion pair, respectively, $[P^-]$ and $[P^-(C^+)]$ are the concentrations of the free ion and ion pair, and $[M]$ is the monomer concentration. C^+ in the above notation is the positive gegenion. Comparison of Eqs. 5-83 and 5-84 yields the apparent k_p as

$$k_p^{app} = \frac{k_p^-[P^-] + k_p^+[P^-(C^+)]}{[M]} \quad (5-85)$$

The two propagating species are in equilibrium according to



governed by the dissociation constant K given by

$$K = \frac{[P^-][C^+]}{[P^-(C^+)]} \quad (5-87)$$

For the case where $[P^-] = [C^+]$, that is, there is no source of either ion other than $P^-(C^+)$, the concentration of free ions is

$$[P^-] = (K[P^-(C^+)])^{1/2} \quad (5-88)$$

The extent of dissociation is small under most conditions, the concentration of ion pairs is close to the total concentration of living ends and Eq. 5-88 can be rewritten as

$$[P^-] = (K[M])^{1/2} \quad (5-89)$$

The concentration of ion pairs is given by

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$$[P^-(C^+)] = [M^-] - (K[M])^{1/2} \quad (5-90)$$

Combination of Eqs. 5-85, 5-89, and 5-90 yields k_p^{app} as a function of $[M]$

$$k_p^{app} = k_p^- + \frac{(k_p^+ - k_p^-)K^{1/2}}{[M]^{1/2}} \quad (5-91)$$

Polymerizations can also be carried out in the presence of excess gegenion by adding a strongly dissociating salt (e.g., $NaBO_3$ to supply excess Na^+). The concentration of free ions, depressed by the common ion effect, is given by

$$[P^-] = \frac{K[M]}{[C^+]} \quad (5-92)$$

When the added salt is strongly dissociated and the ion pairs slightly dissociated, the gegenion concentration is very close to that of the added salt $[CZ]$

$$[C^+] \approx [CZ] \quad (5-93)$$

The concentrations of free anions and ion pairs are given by

$$[P^-] = \frac{K[M]}{[CZ]} \quad (5-94)$$

$$[P^-(C^+)] = [M^-] - \frac{K[M]}{[CZ]} \quad (5-95)$$

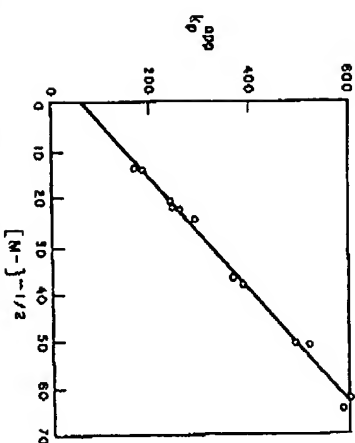


Fig. 5-5. Polymerization of styrene by sodium naphthalene in 2-methyltetrahydrofuran at 20°C. After [132] by permission of Pergamon Press Ltd., Oxford.

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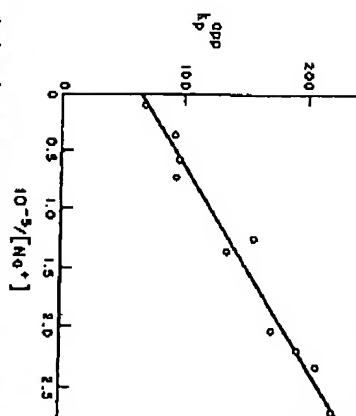


Fig. 5-8. Polymerization of styrene by sodium naphthalene in 3-methyltetrahydrofuran at 20°C in the presence of sodium tetraphenylborate. After [132] (by permission of Pergamon Press Ltd., Oxford).

which are combined with Eq. 5-85 to yield

$$k_p^{\text{app}} = k_p^* + \frac{(k_p^* - k_p^{\text{app}})K}{[CZ]} \quad (5-96)$$

Equations 5-91 and 5-96 allow one to obtain k_p^* , k_p^{app} , and K from k_p^{app} values obtained in the absence and presence of added common ion. A plot of k_p^{app} obtained in the absence of added common ion vs $[M^-]^{1/2}$ yields a straight line whose slope and intercept are $(k_p^* - k_p^{\text{app}})K$ and k_p^* , respectively. A plot of k_p^{app} obtained in the presence of added common ion vs $[CZ]^{-1}$ yields a straight line whose slope and intercept are $(k_p^* - k_p^{\text{app}})K$ and k_p^* , respectively. Figures 5-5 and 5-6 show these plots for polystyryl sodium in 3-methyltetrahydrofuran at 20°C [132]. The combination of the two slopes and two intercepts allows the individual calculation of k_p^* , k_p^{app} , and K .

5-3d-2-5. *Reactivity in Anionic Polymerization.* Table 5-10 shows the values of K and the propagation rate constants for free ions and ion pairs in styrene polymerization in THF at 25°C with various alkali metal cations [133, 134]. The corresponding k_p^* values in dioxane are also presented. K and k_p^* values could not be obtained; conductivity measurements showed there is no detectable dissociation of ion pairs to free ions in dioxane. A consideration of the data in Table 5-10 allows an understanding of reactivity in anionic polymerization. The data for polymerization in THF show the much greater reactivity of the free ion compared to any of the ion pairs. The value of k_p^* is 6.5×10^4 liter/mole-sec, which is larger by a factor of 10^2 than the k_p^* values. The higher reactivity of the free ion is not un-

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Table 5-10. Effect of Gegenion on Anionic Polymerization of Styrene^a

Gegenion	Polymerization in Tetrahydrofuran		k_p^* for Dioxane
	k_p^*	$K \times 10^1$	
Li ⁺	160	2.2	0.94
Na ⁺	80	1.5	3.4
K ⁺	60-80	0.8	19.8
Rb ⁺	50-80	0.1	21.5
Cs ⁺	22	0.02	24.5

^a Data from [133] and [134].

equivocally expected. It does indicate that the most important factor determining reactivity is polarization of the π electrons of a monomer molecule by the electric field generated by the propagating carbonion's charge [110, 111]. A *push-pull* mechanism is probably operative in propagation by ion pairs. The gegenion pulls on the nucleophile, while the carbonion center pushes, simultaneously, the bond between the gegenion and carbonion stretches sufficiently for monomer to be inserted (added) between them. That free ions are more reactive than ion pairs indicates that the driving force due to the pull of the gegenion is not the major factor in determining ion-pair reactivity. If it were the major factor and it were sufficiently large, ion pairs might be more reactive than free ions.

The K values in Table 5-10 indicate clearly that increased solvating power affects the reaction rate primarily through an increase in the concentration of free ions. When lithium is the gegenion, about 1½% of the propagating centers in THF (for a system containing 10^{-3} molar initiator) are free ions compared to none in dioxane. Since free ions are so much more reactive than ion pairs, this small concentration has a very large effect on the observed polymerization rate. The majority of the propagation is carried by free ions; only about 10% of the observed rate is due to ion pairs. It is worth mentioning that K values independently measured by conductivity are in excellent agreement with those obtained from the kinetic measurements. K from conductivity is 1.9, 1.5, 0.7, and 0.028, respectively, for lithium, sodium, potassium, and cesium gegenions [130, 135, 136]. Table 5-10 shows that the dissociation constant for the ion pair decreases in going from lithium to cesium as the gegenion. The order of increasing K is the order of increasing solvation of the gegenion. The smaller Li⁺ is solvated to the greatest extent and the larger Cs⁺ is the least solvated. The decrease in K has a very significant effect on the overall polymerization, since there is a very significant change in the concentration of the highly reactive free ions. Thus the free ion concentration for polystyryl cesium ($K = 0.02 \times 10^{-1}$) is less than 10% that of polystyryl lithium ($K = 2.2 \times 10^{-1}$).

The reactivities of the various ion pairs also increase in the same order as the K values: Li > Cs. The fraction of the ion pairs that are of the solvent-separated type increases with increasing solvation of the gegenion. Solvent-separated ion pairs are much more reactive than contact ion pairs (Sec. 5-3d-4). The lower values of k_p^* in dioxane relative to THF are also a consequence of there being a higher fraction of

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the more reactive solvent-separated ion pairs. The order of reactivity for the different ion pairs in dioxane is the reverse of that in tetrahydrofuran. Solvation is not important in dioxane. The ion pair with the highest reactivity is that with the weakest bond between the carbanion center and pyridine. The bond strength decreases and reactivity increases with increasing size of pyridine. The push-pull type of propagation, with monomer insertion between the carbanion and pyridine is facilitated by a decrease in the bond strength between the two ionic charges [111].

5.3d.3 Degree of Polymerization

The number-average degree of polymerization for a living polymer is given simply by the ratio of the concentrations of monomer and living ends,

$$\bar{X}_n = \frac{[M]}{[M^-]} \quad (5.97)$$

For the usual situation where all of the initiator I is converted into propagating living anionic ends, Eq. 5.97 becomes

$$\bar{X}_n = \frac{2[M]}{[I]} \quad (5.98)$$

or

$$\bar{X}_n = \frac{[M]}{[I]} \quad (5.99)$$

depending on the mode of initiation. Equation 5.98 applies to polymizations initiated by electron transfer since each final polymer molecule originates from two initiator molecules (via the dianionic propagating species). Initiation processes other than electron transfer (e.g., butyllithium) involve one polymer molecule per initiator molecule and Eq. 5.99 is applicable.

A consequence of the absence of a termination reaction in the polymerization is that the polymer produced should be essentially monodisperse (that is, $\bar{M}_w/\bar{M}_n \approx \bar{X}_n$) under certain conditions. Efficient mixing throughout the polymerization is required. Depropagation must be slow compared to propagation. Initiation must be reasonably fast relative to propagation so that all of the active centers begin to propagate almost simultaneously; all polymer molecules will grow for close to the same length of time. The size distribution will specifically be given by the Poisson distribution [110,138,139]

$$\frac{\bar{X}_w}{\bar{X}_n} = 1 + \frac{\bar{X}_n}{(\bar{X}_n + 1)^2} \quad (5.100a)$$

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which can be approximated by

$$\frac{\bar{X}_w}{\bar{X}_n} \approx 1 + \frac{1}{\bar{X}_n} \quad (5.100b)$$

Equation 5.100 shows that for any but a very low molecular weight polymer, the size distribution will be very narrow with \bar{X}_w/\bar{X}_n (-PDI) being close to unity. For a polymer of an average molecular weight of 500,000 having a Poisson distribution, 95% of all molecules will have molecular weights within 10% of the average; PDI would be 1.002. Polymers having very close to this PDI value have been synthesized by the living polymerization technique. Thus PDI is in the range 1.06-1.12 for styrene polymerization by sodium naphthalene [110]. The living polymer technique offers a unique method of synthesizing standard polymer samples of known and well defined molecular weights. Commercially available polystyrene standards are used extensively in molecular weight measurements by gel permeation chromatography, osmometry, viscometry, and cryoscopy.

The occurrence of any termination or side reactions does result in broadening of the molecular weight distribution. The intramolecular association of dianion propagating centers simultaneously with conversion of some dianions to monocations by side reactions impurities is reported to yield two types of propagating centers propagating at different rates under certain conditions [140,141]. The termination reactions in methyl methacrylate (Sec. 5.3b.4) [122] and depropagation in α -methylstyrene [142,143] broaden the molecular weight distribution.

The large difference in reactivity between free ions and ion pairs appears to contradict a requirement for the Poisson distribution, that all chains grow for the same length of time. However, there is usually a rapid equilibrium between free ions and ion pairs and sharp molecular weight distributions are obtained. A polymer chain propagates both as free ion and ion pair over its lifetime and, on the average, the fractions of its lifetime spent as a free ion and ion pair are not too different than for any other propagating chain. What small differences exist in any system may give rise to some broadening of the MWD, but this can be overcome by adding an inert common-ion salt to suppress the free ion propagation [144].

5.3d.4 Energetics, Solvent-Separated and Contact Ion Pairs

The data available on the temperature dependence of the rates of living polymerization show the experimental activation energy E_a is generally relatively low and positive. One should note that E_a for living polymerization is the activation energy for propagation. The polymerization rates are relatively insensitive to temperature but increase with increasing temperature. Furthermore, the activation energy varies considerably depending on the solvent employed in the polymerization as was the case for cationic polymerization. Thus the activation energy for propagation in the system styrene-sodium naphthalene is 37.6 kJ/mole in dioxane and only 4.2 kJ/mole in tetrahydrofuran [130,145,146]. The molecular weight of the polymer produced in a nontermination polymerization is unaffected by temperature if trans-

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